PATENT SPECIFICATION

Inventor: ERNEST AUGUSTUS SAXON-NAPIER

790,306

Date of filing Complete Specification: Aug. 29, 1955.

Application Date: Aug. 28, 1954. *No. 25044/54.*

Complete Specification Published: Feb. 5, 1958.

Index at acceptance:—Class 91, D2(C: F: G: H: L: N: P: S: W), S2(C: F: G: H:L: N: P: S: W).

International Classification:—C11d.

COMPLETE SPECIFICATION

Cleaning Compositions for Surfaces Contaminated with Heavy Metal Compounds

ERRATA

SPECIFICATION No. 790,306

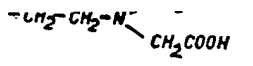
Page 1, line 60, *for* "(the product then amine tetra-acetic ethylenedi-acid)" *read* "(the product then being ethylenediamine tetra-acetic acid)"

Page 2, line 2, *for* "disodium" *read* "di-sodium"

THE PATENT OFFICE,
9th June, 1958.

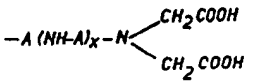
metal salt, on account of the difficulty of maintaining adequate amounts of such comparatively fluid materials at the affected point. Furthermore, complexing agents of this type are not soluble in organic liquids and therefore cannot be made ingredients of decontaminating creams based on fat, lanolin, or the like fatty emolient. We have also found, somewhat surprisingly, that an emulsion cream containing a fatty oil and an aqueous solution of such a complexing agent is quite ineffective as a decontaminating agent for radioactive and other heavy metal deposits.

According to the present invention there is provided an aqueous cleansing cream comprising an alkali metal or ammonium or substituted ammonium (including alkylolamine) salt of a polyamino-polycarboxylic acid (or nitrilotriacetic acid) complexing agent or of an alkaline earth metal complex thereof, water and a water-soluble polymer known to give aqueous solutions of high viscosity, the com-



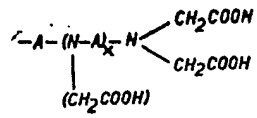
being ethylenediacid)

(3)



or

(4)



(x being 0 or a positive integer and A being an alkylene or hydroxyalkylene group).

The salt employed in the cleansing cream of the present invention may be, for example, the di-, tri- or tetra-sodium or potassium salt,

[*Price 3s 6d*] Price 4s 6d

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International Classification:—C11d.

COMPLETE SPECIFICATION

Cleaning Compositions for Surfaces Contaminated with Heavy Metal Compounds

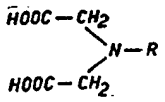
We, BRENTFORD SOAP COMPANY LIMITED, a British Company, of Brent Works, Brentford, Middlesex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods of and compositions for removing deposits of heavy metal compounds, and in particular deposits of radioactive materials, such as fission products from an atomic pile, from surfaces, including laboratory and industrial equipment, clothing and human skin.

The usefulness of complexing agents, particularly organic complexing agents of the polyamino polycarboxylic acid type for such purposes is well-known and has been described, for example, in "Industrial and Engineering Chemistry," 1950, *42*, pages 1469 and 1475. It is, however, often unsatisfactory to apply such compounds in the most usual form, i.e. as an aqueous solution of an alkali metal salt, on account of the difficulty of maintaining adequate amounts of such comparatively fluid materials at the affected point. Furthermore, complexing agents of this type are not soluble in organic liquids and therefore cannot be made ingredients of decontaminating creams based on fat, lanolin, or the like fatty emolient. We have also found, somewhat surprisingly, that an emulsion cream containing a fatty oil and an aqueous solution of such a complexing agent is quite ineffective as a decontaminating agent for radioactive and other heavy metal deposits.

According to the present invention there is provided an aqueous cleansing cream comprising an alkali metal or ammonium or substituted ammonium (including alkylolamine) salt of a polyamino-polycarboxylic acid (or nitrilotriacetic acid) complexing agent or of an alkaline earth metal complex thereof, water and a water-soluble polymer known to give aqueous solutions of high viscosity, the composition being substantially free from any derivative of a fatty acid amide of which said fatty acid contains at least 8 carbon atoms in the molecule. The cream may also include a polyhydric alcohol such as glycerol, and/or in some cases a lower aliphatic alcohol such as methylated spirit.

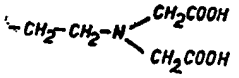
The polycarboxylic acid complexing agent may be, for example, ethylenediamine tetra-acetic acid. In general, it has the formula



wherein R is either

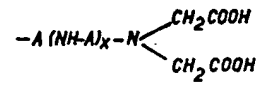
(1) $-CH_2COOH$ (the product then being nitrilotriacetic acid)

(2)



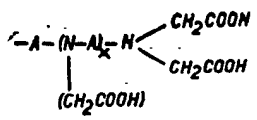
(the product then being ethylenediamine tetra-acetic acid)

(3)



or

(4)



(x being 0 or a positive integer and A being an alkylene or hydroxyalkylene group).

The salt employed in the cleansing cream of the present invention may be, for example, the di-, tri- or tetra-sodium or potassium salt,

[*Price 3*] Price 4s 6d

Price 4s 6d

the di- or tri-ammonium salt, the tri-triethanolamine salt, or disodium or di-potassium calcium complex of ethylenediamine tetra-acetic acid or the di-ammonium or tri-sodium or tri-potassium salt of nitrilo-triacetic acid.

The water-soluble polymer known to confer high viscosity on its aqueous solutions may be, for example, sodium alginate, polyvinyl alcohol, carboxymethylcellulose sodium salt or a water-soluble gum or mucilage such as gum tragacanth.

We have found that the di-alkali metal, di-amine or di-ammonium salts of ethylene di-amine tetra-acetic acid are even more effective in removing heavy metal compounds from surfaces than the tri- or tetra-salts of this acid, and that in particular the di-ammonium salt of ethylene diamine tetra-acetic acid is outstanding in its capacity for removing mixed fission products, particularly radio-isotopes of rare earth elements, from laboratory equipment. Since the di-salts referred to are mildly acid (giving solution pH of about 4—5), it is advisable in formulating decontaminating creams based upon them to avoid the use of ionisable thickening agents such as sodium alginate from which the corresponding acid may be precipitated by the complexing agent. In such cases, the preferred thickening agents are polyvinyl alcohol and water-soluble gums, paricularly gum tragacanth.

It has also been found that sodium alginate is not very effective for thickening creams containing the tetra-sodium or tetra-potassium salt of ethylene diamine tetra-acetic acid, the alkaline pH of the complexing agent causing the partial "salting out" of the stiffening agent in this case. No such salting out was observed with carboxymethyl cellulose sodium salt; however, the complexing agent decreased the effectiveness of carboxymethyl cellulose sodium salt relative to its effectiveness in pure water, to a marked extent even at 5% of the complexing agent, and more so at higher concentrations. This applies alike to the di-, tri- and tetra-salts of ethylene diamine tetra-acetic acid. However, by using a much larger amount of carboxymethyl cellulose sodium salt than required with pure water, a cream incorporating such a salt of the amino acid and with comparable viscosity can be produced. Thus when using the more alkaline complexing agents, non-ionic gums are preferred as thickening agents.

The rapidity of action and effectiveness of the decontaminating creams of the present invention naturally increases with their content of complexing agent and is thus only limited by the water-solubility of the latter. For this reason also we particularly prefer the use of the di-ammonium salt of ethylene di-amine tetra-acetic acid, since this is much more soluble in water than the corresponding sodium salt (i.e. to the extent of about 45% as against about 15% at 25°C).

At least 2% of the complexing agent should suitably be used on the total weight of composition, and we prefer the use of at least 5%, the upper limit being in each case that given by the water-solubility of the particular poly-amino polycarboxylic acid derivative used.

The proportion of thickening agent used should be such as to give a product having the consistency of thick cream rather than a solid gel. Usually, about 3—5% of sodium alginate, for example, or about 1—3% of gum tragacanth, suffices for this purpose. Up to 10% of glycerol or other polyhydric alcohol may be added if desired. Except when a lower aliphatic alcohol is present, the ingredients are preferably mixed at an elevated temperature. This temperature is not critical. In general, higher temperatures facilitate the production of the cream but care has to be taken to avoid water loss which may easily occur at temperatures above about 60°—70°C.

The aqueous cleansing cream is useful for the decontamination of the human skin when such skin has become contaminated by heavy metals, especially radioactive materials. For this purpose it is first smeared over the skin and then flushed away with water. The complexing agent is less absorbed by the human skin from an aqueous cream than from a fluent aqueous solution.

The aqueous cleansing cream is also useful for the decontamination of the solid surfaces such as those of machines, instruments and apparatus when such surfaces have become contaminated by heavy metals, especially radioactive materials. The present invention accordingly includes the method of decontaminating such surfaces which consists in applying to such surfaces an aqueous cleansing cream according to the present invention and then flushing the cream-coated surfaces with water until the cream has been removed.

By using an aqueous cleansing cream it is possible to secure a very high local concentration of the complexing agent on the surface to be treated, much higher than if a fluent aqueous solution is applied to the surface.

The invention will be illustrated by, but is not limited to, the following examples.

Example 1

Sodium alginate (4 parts) was gradually added to water (76 parts) with constant stirring, until a homogeneous solution was obtained. This was allowed to stand for 12 hours and 20 parts of the tri-sodium salt of ethylene di-amine tetra-acetic acid was then added with heating. The temperature is not critical but undue water loss must be avoided. The resulting cream, containing 20% of tri-sodium salt of ethylene diamine tetra-acetic acid, was several times as effective as a 20% aqueous solution of the same salt, in removing mixed fission products from glass surfaces.

EXAMPLE 2

Sodium alginate (4 parts) was wetted with glycerol (8 parts) and boiling water (68 parts) was stirred into the wetted sodium alginate. 20 parts of the tri-sodium salt of ethylene diamine tetra-acetic acid was then added, to give a cream similar in effectiveness to that of Example 1.

EXAMPLE 3

Gum tragacanth (2 parts) and glycerol (4 parts) were mixed to form a paste and to this was gradually added, with stirring, a solution of 20 parts of the tri-sodium salt of ethylene diamine tetra-acetic acid in 74 parts of hot water. After thorough stirring, the cream was allowed to stand for 12 hours and then further stirred to homogeneity. A cream similar in effectiveness to that of Example 1 was produced. As in the case of Example 1, the temperature is not critical but undue water loss must be avoided.

EXAMPLE 4

As in Example 3, but a solution of 5 parts of the di-sodium salt of ethylene diamine tetra-acetic acid in 89 parts of water was substituted for the solution referred to therein. A cream of very similar effectiveness was obtained.

EXAMPLE 5

As in Example 4, but 5 parts of the di-ammonium salt of ethylene diamine tetra-acetic acid was substituted for the di-sodium salt. A cream of substantially greater effectiveness was obtained.

EXAMPLE 6

As in Example 4, but 5 parts of the di-sodium calcium complex of ethylene diamine tetra-acetic acid was substituted for the di-sodium salt. A cream having substantially no action on body calcium was thus obtained.

It has been found useful to include in these creams a wetting agent such as liquid soap or a synthetic aliphatic sulphate compound such as that sold under the Registered Trade Mark "Teepol." The latter is more satisfactory, giving a clear cream. Liquid soap tends to produce a cloudy cream. The gum and glycerol are first stirred together to a paste. About half the water is then stirred in, followed by a hot solution of the ethylene-diamine tetra-acetic acid salt in the remainder of the water and then the wetting agent.

In the examples utilising gum tragacanth, glycerol can in general be replaced by a lower aliphatic alcohol, as for instance, methylated spirit. The use of spirit improves the ease of manufacturing the cream, circumventing lump formation. For this purpose as low a proportion as 3 parts of alcohol to 2 parts of gum are satisfactory, although lower and higher proportions of alcohol can be used, 2 parts to 1 part of gum being suggested here. Using this method a cold ethylene diamine tetra-acetic acid salt solution must be quickly added to the gum-alcohol mixture and stirred until the consistency no longer changes. Heating is unnecessary. No lumps are formed and the 12 hour standing before stirring to homogeneity becomes unnecessary.

EXAMPLE 7

A cream containing 2 parts gum tragacanth, 4 parts of glycerol or ethyl alcohol, 5 parts of the diammonium salt of ethylene diamine tetra-acetic acid, 1 part of Teepol and 78 parts of water, was produced by any of the methods described in Example 3, or after. 10 parts of Kieselguhr were then stirred into the smooth cream.

EXAMPLE 8

A cream containing 2 parts of gum tragacanth, 4 parts of glycerol or ethyl alcohol, the equivalent of 1 part of sodium silicate, for instance $2\frac{1}{3}$ parts metasilicate of soda ($Na_2SiO_3 9H_2O$), 20 parts of the tetra-sodium salt of ethylene diamine tetra-acetic acid and $70\frac{2}{3}$ parts of water, was made by the method of any of the preceding Examples. In this case a solution of the silicate in 10 parts of water was stirred into the gum-alcohol or glycerol mixture, quickly followed by a solution of the sodium salt of the amino acid in $60\frac{2}{3}$ parts of water.

EXAMPLE 9

A cream as Example 8, replacing the 1 part of sodium silicate by 1 part of Magnesium silicate made in situ. The gum (2 parts) and ethyl alcohol or glycerol (4 parts) were mixed, 2.84 parts of metasilicate of soda in 8.7 parts of water were stirred in, quickly followed by 2.46 parts of magnesium sulphate ($MgSO_4.7H_2O$) in 10 parts of water, rapidly followed by the sodium salt of the amino acid, dissolved in 50 parts of water.

The creams in Examples 8 and 9 will not attack aluminium surfaces which are ordinarily quickly and extensively attacked.

Creams of the type described so far can be used for other purposes than removing heavy metal compound contamination. For instances, scales can be removed from surfaces, or "beerstone" which is essentially calcium oxalate from brewery vats. In such cases where creams usually have to be left on surfaces for longer periods of time it is advisable to use thicker creams containing 4 to 5, or even more, per cent of gum tragacanth (percentage in respect to the amount of water used), and larger percentages of the complexing agent, which in this case, is preferably the tetra-sodium salt of ethylene diamine tetra-acetic acid, the upper limit being given by the solubility of the salt in the amount of water used in the cream.

We make no claim herein to a detergent solution, suitable for removing radioactive contamination from objects and materials, comprising a synthetic surface active agent, a small amount of ethylenediamine tetra-acetic acid and another polycarboxylic acid in aqueous solution, such a detergent solution

being described and claimed in Specification No. 763547.

What we claim, subject to the foregoing disclaimer, is:—

1. An aqueous cleansing cream comprising an alkali metal or ammonium or substituted ammonium (including alkylolamine) salt of a polyamino-polycarboxylic acid (or nitrilotriacetic acid) complexing agent or of an alkaline earth metal complex thereof, water and a water-soluble polymer known to give aqueous solutions of high viscosity, the composition being substantially free from any derivative of a fatty acid amide of which said fatty acid contains at least 8 carbon atoms in the molecule.

2. An aqueous cleansing cream as claimed in claim 1 in which the polyamino polycarboxylic acid complexing agent is ethylene diamine tetra-acetic acid.

3. An aqueous cleansing cream as claimed in claim 2 in which a di-alkali metal, diamine or di-ammonium salt of ethylenediamine tetra-acetic acid is used.

4. An aqueous cleansing cream as claimed in any of claims 1 to 3 in which the water-soluble polymer is polyvinyl alcohol or a water-soluble gum.

5. An aqueous cleansing cream as claimed in any of claims 1 to 3 in which the water-soluble polymer is gum tragacanth.

6. An aqueous cleansing cream comprising the di-ammonium salt of ethylenediamine tetra-acetic acid, water and gum tragacanth.

7. An aqueous cleansing cream as claimed in claim 5 or 6 which also includes a lower aliphatic alcohol.

8. An aqueous cleansing cream comprising the tri-sodium or tri-potassium salt of ethylenediamine tetra-acetic acid and sodium alginate.

9. An aqueous cleansing cream comprising the tri-sodium or tetra-sodium or tri-potassium or tetra-potassium salt of ethylene diamine tetra-acetic acid and the sodium salt of carboxymethyl cellulose.

10. An aqueous cleansing cream as claimed in any of the preceding claims in which the amount of salt or complex salt of polyamino polycarboxylic acid complexing agent is at least 5% of the total weight.

11. An aqueous cleansing cream as claimed in any of the preceding claims which also includes a polyhydric alcohol, such as glycerol.

12. An aqueous cleansing cream as claimed in any of the preceding claims which also includes sodium or magnesium silicate.

13. Aqueous cleansing creams as herein particularly described and illustrated by the examples.

14. The method of decontaminating a surface when such surface has become contaminated by heavy metals, especially radioactive materials, which consists in applying to such surface an aqueous cleansing cream as claimed in any of claims 1 to 13 and then flushing the cream-coated surface with water until the cream has been removed.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

PROVISIONAL SPECIFICATION

Cleaning Compositions for Surfaces Contaminated with Heavy Metal Compounds

We, BRENTFORD SOAP COMPANY LIMITED, a British Company, of Brent Works, Brentford, Middlesex, do hereby declare this invention to be described in the following statement:—

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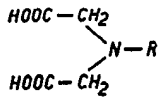
The usefulness of complexing agents, particularly organic complexing agents of the polyamino polycarboxylic acid type for such purposes is well-known and has been described, for example, in "Industrial and Engineering Chemistry," 1950, *42*, pages 1469 and 1475. It is, however, often unsatisfactory to apply such compounds in the most usual form, i.e., of an aqueous solution of their alkali metal salts, on account of the difficulty of maintaining adequate amounts of such comparatively fluid materials at the affected point. Furthermore, complexing agents of this type are not soluble in organic liquids and therefore cannot be made ingredients of decontaminating creams based on fat, lanolin, or the like fatty emolient. We have also found, somewhat surprisingly, that an emulsion cream containing a fatty oil and an aqueous solution of such a complexing agent is quite ineffective as a decontaminating agent for radioactive and other heavy metal deposits.

According to the present invention there is provided an aqueous cleansing cream comprising an alkali metal or ammonium or substituted ammonium (including alkylolamine) salt or an alkaline earth metal complex of a polyamino polycarboxylic acid complexing agent, water and a water-soluble polymer known to confer high viscosity on its aqueous solutions. The cream may also include a polyhydric alcohol such as glycerol.

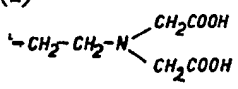
The polycarboxylic acid complexing agent

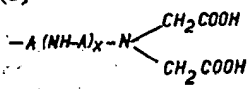
may be, for example, ethylenediamine tetra-acetic acid. In general, it has the formula

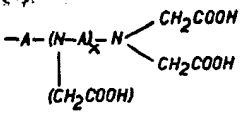


wherein R is either

(1) —CH_2COOH (the product then being nitrilotriacetic acid)

(2)  (the product then being ethylenediamine tetra-acetic acid)

(3)  or

(4) 

(x being 0 or a positive integer and A being an alkylene or hydroxylkylene group).

The salt employed in the cleansing cream of the present invention may be the di-, tri- or tetra-sodium or potassium salt, the di-, or tri-ammonium salt, the tri-triethanolamine salt, or the di-sodium or di-potassium calcium complex of ethylene diamine tetra-acetic acid or the di-ammonium or tri-sodium or tri-potassium salt of nitrilo-triacetic acid.

The water-soluble polymer known to confer high viscosity on its aqueous solutions may be, for example, sodium alginate, polyvinyl alcohol, carboxymethylcellulose sodium salt or a water-soluble gum or mucilage such as gum tragacanth.

We have found that the di-alkali metal, di-amine or di-ammonium salts of ethylene di-amine tetra-acetic acid are even more effective in removing heavy metal compounds from surfaces than the tri- or tetra-salts of this acid, and that in particular the di-ammonium salt of ethylene diamine tetra-acetic acid is outstanding in its capacity for removing mixed fission products, particularly radio-isotropes of rare earth elements, from laboratory equipment. Since the di-salts referred to are mildly acid (giving solution pH of about 4—5), it is advisable in formulating decontaminating creams based upon them to avoid the use of ionisable thickening agents such as sodium alginate or carboxymethyl cellulose sodium salt, from which the corresponding acid may be precipitated by the complexing agent. In such cases, the preferred thickening agents are polyvinyl alcohol and water-soluble gums, particularly gum tragacanth.

The rapidity of action and effectiveness of the decontaminating creams of the present invention naturally increases with their content of complexing agent and is thus only limited by the water-solubility of the latter. For this reason also we particularly prefer the use of the di-ammonium salt of ethylene di-amine tetra-acetic acid, since this is much more soluble in water than the corresponding sodium salt (i.e. to the extent of about 45% as against about 15% at 25°C).

At least 2% of the complexing agent should suitably be used on the total weight of composition, and we prefer the use of at least 5%, the upper limit being in each case that given by the water-solubility of the particular polyamino polycarboxylic acid derivative used.

The proportion of thickening agent used should be such as to give a product having the consistency of thick cream rather than a solid gel. Usually, about 3—5% of sodium alginate, for example, or about 1—3% of gum tragacanth, suffices for this purpose. Up to 10% of glycerol or other polyhydric alcohol may be added if desired. The invention is illustrated by the following examples.

The invention includes the method of decontaminating surfaces, including the body surface of human beings and other living animals, when such surfaces have become contaminated by heavy metals especially radio-active materials, which consists in applying to such surfaces an aqueous cleansing cream according to the present invention and then flushing the cream-coated surfaces with water until the cream has been removed.

By this method it is possible to secure a very high local concentration of the complexing agent on the surface to be treated, much higher than if a fluent aqueous solution is applied to the surface. Moreover, the complexing agent is less absorbed by the human skin from an aqueous cream than from a fluent aqueous solution. The temperature of heating is not critical. In general, higher temperatures facilitate the production of the cream but care has to be taken to avoid water loss which may easily occur at temperatures above about 60°—70°C.

EXAMPLE 1.

Sodium alginate (4 parts) was gradually added to water (76 parts) with constant stirring, until a homogeneous solution was obtained. This was allowed to stand for 12 hours and 20 parts of the tri-sodium salt of ethylene di-amine tetra-acetic acid was then added with heating. The resulting cream, containing 20% of tri-sodium salt of ethylene diamine tetra-acetic acid, was several times as effective as a 20% aqueous solution of the same salt, in removing mixed fission products from glass surfaces.

EXAMPLE 2.

Sodium alginate (4 parts) was wetted with glycerol (8 parts) and boiling water (68 parts) was stirred into the wetted sodium alginate. 20 parts of the tri-sodium salt of ethylene diamine tetra-acetic acid was then added, to give a cream similar in effectiveness to that of Example 1.

EXAMPLE 3.

Gum tragacanth (2 parts) and glycerol (4 parts) were mixed to form a paste and to this was gradually added, with stirring, a solution of 20 parts of the tri-sodium salt of ethylene diamine tetra-acetic acid in 74 parts of hot water. After thorough stirring, the cream was allowed to stand for 12 hours and then further stirred to homogeneity. A cream similar in effectiveness to that of Example 1 was produced. As in the case of Example 1, and for the same reasons, the temperature is not critical but undue water loss must be avoided.

EXAMPLE 4.

As in Example 3, but a solution of 5 parts of the di-sodium salt of ethylene diamine tetra-acetic acid in 89 parts of water was substituted for the solution referred to therein. A cream of very similar effectiveness was obtained.

EXAMPLE 5.

As in Example 4, but 5 parts of the di-ammonium salt of ethylene diamine tetra-acetic acid was substituted for the di-sodium salt. A cream of substantially greater effectiveness was obtained.

EXAMPLE 6.

As in Example 4, but 5 parts of the di-sodium calcium complex of ethylene diamine tetra-acetic acid was substituted for the di-sodium salt. A cream having substantially no action on body calcium was thus obtained.

It has been found convenient, when making creams containing a higher proportion of gum tragacanth than in Examples 3 to 6, for example 5%, to include a wetting agent such as liquid soap or a synthetic aliphatic sulphate compound such as that sold under the Trade Mark "Teepol." The latter is more satisfactory, giving a clear cream. Liquid soap tends to produce a cloudy cream. The gum, glycerol and wetting agent are first stirred together to a paste. About half of the water is then stirred in, followed by a hot solution of the ethylene-diamine tetra-acetic acid salt in the remainder of the water.

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Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.